

On a Thomas-Fermi model of "hollow" atom

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Abstract

A Thomas-Fermi model of a spherical shell of positive charge is investigated, under various boundary conditions. The electron distribution and the ionization charge are given particular attention.

The advent of the fullerene molecule[1] and the metallic clusters[2] have called the attention upon the stability of new atomic micro-objects. One of them is described in this paper. As it is known, the fullerene molecule C_{60} consists of 60 carbon atoms (C), arranged (in pentagons and hexagons) on the surface of a sphere of radius $\sim 3.5 \text{ \AA}$. Certain clusters, made of (relatively) a small number of atoms (as, for example, alkali atoms), have been identified in solid-state matrices, particularly in the octahedral interstices of face-centered cubic fullerites. They acquire regular geometrical shapes, like tetrahedrons, or cubes, the latter being sometimes centered. We investigate herein the stability of a Thomas-Fermi model suggested by these micro-objects.

As it is known, the Thomas-Fermi model starts with free electrons and assumes that, due to the Pauli exclusion principle, there is a certain scale length over which their number, and their effective interaction, vary slowly. It is a quasi-classical theory, and its validity is ensured by the number of electrons being much greater than unity. Of course, at infinitely long distances the theory is not valid, nor at very short distances where the Coulomb potential is singular. In the case of an atom with the atomic number Z we know that the Thomas-Fermi model is not valid for distances shorter than $\sim 1/Z$. As in our case of the micro-objects presented above we are interested in distances of the order of the size of large molecules, or of the order of the solid-state distances, we may also neglect the variations over atomic scale lengths, *i.e.* over the Bohr radius $a_H = \hbar^2/me^2 = 0.53 \text{ \AA}$ (where m is the electron mass, e is the electron charge and \hbar is the Planck's constant). This allows one to treat the atoms in the above micro-objects as being uniformly distributed over a spherical shell of radius R . In addition, one may assume that the centre of the sphere is occupied by a nucleus of positive charge z_0 .

A positive charge z uniformly distributed over the surface of a sphere of radius R , and a central positive charge z_0 , create an electric potential

$$V_1(r) = z/R + z_0/r \quad , \quad r < R \quad , \quad (1)$$

and

$$V_2(r) = (z + z_0)/r \quad , \quad r > R \quad . \quad (2)$$

An electric field

$$E_s = (z/2 + z_0)/R^2 \quad (3)$$

acts outwardly on the spherical surface, which tends to blow the sphere up;

and the electrostatic energy of the object is

$$\mathcal{E}_0 = z(z/2 + z_0)/R \quad . \quad (4)$$

The density of free electrons n is related by the Fermi wavevector k_F through $n = k_F^3/3\pi^2$; the local energy of the electrons should be a constant, for equilibrium,

$$\frac{\hbar^2}{2m}k_F^2 - e\varphi - eV = \text{const} \quad , \quad (5)$$

where φ is the electrostatic potential of the electron distribution, and $V = V_{1,2}$ for $r < R$ and $r > R$, respectively. We shall assume that the electron distribution extends to infinity, in which case $\text{const} = 0$ in (5). We shall also use the atomic units a_H and $e^2/a_H = 27.2 \text{ eV}$, which together with $\hbar = 1$ give $m = 1$ and $e^2 = 1$. Then, from (5), we have

$$n = \frac{2\sqrt{2}}{3\pi^2}(\varphi + V)^{\frac{3}{2}} \quad (6)$$

and the Poisson equation reads

$$\Delta(\varphi + V) = 4\pi n = \frac{8\sqrt{2}}{3\pi}(\varphi + V)^{\frac{3}{2}} \quad (7)$$

for $r \neq R$; remark that $\Delta V = 0$. Introducing the reduced variable $x = r/R$ and

$$\varphi + V = \frac{9\pi^2}{128R^4} \frac{\chi}{x} \quad , \quad (8)$$

we get from (7) the Thomas-Fermi equation

$$x^{\frac{1}{2}}\chi'' = \chi^{\frac{3}{2}} \quad . \quad (9)$$

Since n is a continuous function φ and its two first derivatives are continuous; therefore χ has a slope discontinuity (but itself is a continuous function), exactly as the derivative of V . Defining $\chi_1 = \chi$ for $x < 1$ and $\chi_2 = \chi$ for $x > 1$, we have therefore

$$\chi_1(1) = \chi_2(1) \quad . \quad (10)$$

The number $N(x)$ of electrons inside a sphere of radius x is easily obtained from

$$N(x) = 4\pi R^3 \int_0^x dx x^2 n = \frac{9\pi^2}{128R^3} \int_0^x dx (x\chi' - \chi)' \quad , \quad (11)$$

whence

$$N_1(x) = \frac{9\pi^2}{128R^3} [x\chi_1' - \chi_1 + \chi_1(0)] \quad , \quad x < 1 \quad , \quad (12)$$

and

$$N_2(x) = \frac{9\pi^2}{128R^3} \{x\chi_2' - \chi_2 + [\chi_1'(1) - \chi_2'(1)] + \chi_1(0)\} \quad , \quad x > 1 \quad . \quad (13)$$

We remark that $N(x)$ is continuous at $x = 1$, and

$$N(1) = \frac{9\pi^2}{128R^3} [\chi_1'(1) - \chi_1(1) + \chi_1(0)] \quad . \quad (14)$$

As the system extends to infinity we have to assume that $\chi_2(\infty) = 0$ (together with its derivatives), so that the total number of electrons is given by

$$N = \frac{9\pi^2}{128R^3} [\chi_1'(1) - \chi_2'(1) + \chi_1(0)] \quad . \quad (15)$$

The electric field $E_1(x)$ at $x < 1$, and the total charge $q_1(x)$ inside the sphere of radius $x < 1$, are obtained easily from the Gauss' law,

$$4\pi r^2 E_1 = -4\pi R x^2 \frac{\partial}{\partial x} (\varphi_1 + V_1) = 4\pi \frac{9\pi^2}{128R^3} (\chi_1 - x\chi_1') = 4\pi q_1 \quad , \quad (16)$$

whence

$$q_1 = \frac{9\pi^2}{128R^3} (\chi_1 - x\chi_1') \quad , \quad (17)$$

and

$$E_1(x) = \frac{q_1(x)}{R^2 x^2} \quad . \quad (18)$$

Since $q_1 = z_0 - N_1$, we obtain from (12) and (17)

$$z_0 = \frac{9\pi^2}{128R^3} \chi_1(0) \quad . \quad (19)$$

Similarly, the electric field at $x > 1$ is $E_2(x) = q_2(x)/R^2 x^2$ and the charge

$$q_2 = \frac{9\pi^2}{128R^3} (\chi_2 - x\chi_2') \quad , \quad (20)$$

whence, by using (13) and (19), we get

$$z = \frac{9\pi^2}{128R^3} (\chi_1'(1) - \chi_2'(1)) \quad . \quad (21)$$

We remark that (21) expresses exactly the jump in the slope of χ and of V at $x = 1$, as we said above; and the total charge $q = q_2(\infty) = 0$, *i.e.* the infinite system is neutral.

The electrons act on the shell with an electric field E_{el} given by

$$\begin{aligned} E_{el} &= -\frac{\partial\varphi}{\partial r} \Big|_{r=R} = -\frac{9\pi^2}{128R^5} \frac{\partial}{\partial x} \left(\frac{\chi_1}{x} \right) \Big|_{x=1} + \frac{\partial V_1}{\partial r} \Big|_{r=R} = \\ &= -\frac{9\pi^2}{128R^5} [\chi_1'(1) - \chi_1(1)] - \frac{z_0}{R^2} \quad , \end{aligned} \quad (22)$$

or, equivalently,

$$E_{el} = -\frac{9\pi^2}{128R^5} [\chi_2'(1) - \chi_2(1)] - \frac{z + z_0}{R^2} \quad , \quad (23)$$

if we use (10) and (21). From (14) and (19) we find that

$$E_{el} = -N(1)/R^2 \quad , \quad (24)$$

as expected. In order to have the equilibrium of the shell this field must compensate the field E_s given by (3), *i.e.*

$$N(1) = z/2 + z_0 \quad ; \quad (25)$$

or, using (14), (19) and (21),

$$2\chi_1(1) = \chi_1'(1) + \chi_2'(1) \quad . \quad (26)$$

Equations (19) and (21) may be viewed as giving the parameters $z_0 R^3$ and $z R^3$, respectively; therefore, we have to solve the Thomas-Fermi equation (9) under the rather natural conditions $\chi_1(1) = \chi_2(1)$, $\chi_2(\infty) = 0$ and (26). There is no such a solution. We have always, in fact, $2\chi_1(1) > \chi_1'(1) + \chi_2'(1)$, which means that $N(1) < z/2 + z_0$, *i.e.* the electrons inside the sphere are not numerous enough to ensure the equilibrium; due to their fermionic nature they prefer to go outside the sphere where their kinetic energy is lower. The infinite Thomas-Fermi "hollow" atom is too "rarefied" to be stable.

Obviously, the only way to attain the equilibrium of such a "hollow" atom is to embed it into a cage, as, in fact, it is a more realistic case.

Suppose that we have a spherical cage of radius $R_0 > R$, where the "hollow" atom is introduced. The Thomas-Fermi relationship (5) now reads

$$\frac{\hbar^2}{2m} k_F^2 - e\varphi - eV - U = -e\varphi_0 \quad , \quad (27)$$

where U is the potential well of the cage and φ_0 is the chemical potential, which must equal the external potential for preventing the flux of electrons from either going out or in the cage. Introducing the reduced variable $x = r/R_0$ and defining

$$\varphi + V + U - \varphi_0 = \frac{9\pi^2}{128R_0^4} \frac{\chi}{x} \quad (28)$$

(in atomic units) we arrive at the Thomas-Fermi equation (9) with the continuity condition (10) at $a = R/R_0$. The number of electrons (12) and (13) is now given by

$$N_1(x) = \frac{9\pi^2}{128R_0^3} \left[x\chi_1' - \chi_1 + \chi_1(0) \right] \quad , \quad x < a \quad , \quad (29)$$

and

$$N_2(x) = \frac{9\pi^2}{128R_0^3} \left\{ x\chi_2' - \chi_2 + a \left[\chi_1'(1) - \chi_2'(1) \right] + \chi_1(0) \right\} \quad , \quad x > a \quad . \quad (30)$$

Similar relations (17) – (20) hold now, with R replaced by R_0 ; while the discontinuity condition (21) becomes now

$$z = \frac{9\pi^2}{128R_0^3} a \left[\chi_1'(a) - \chi_2'(a) \right] \quad . \quad (31)$$

A similar condition (25) for equilibrium is also obtained. Summing up all these relationships we have to solve the Thomas-Fermi equation $x^{\frac{1}{2}}\chi'' = \chi^{\frac{3}{2}}$ under the following conditions:

$$z_0 = \frac{9\pi^2}{128R_0^3} \chi_1(0) \quad , \quad (32)$$

$$\chi_1(a) = \chi_2(a) \quad , \quad (33)$$

$$z = \frac{9\pi^2}{128R_0^3}a \left[\chi_1'(a) - \chi_2'(a) \right] \quad , \quad (34)$$

$$2\chi_1(a) = a \left[\chi_1'(a) + \chi_2'(a) \right] \quad ; \quad (35)$$

in which case the total charge in the cage is given by

$$q = \frac{9\pi^2}{128R_0^3} \left[\chi_2(1) - \chi_2'(1) \right] \quad . \quad (36)$$

First, we remark that, as we said above, leaving aside (32) and (34), as giving the parameters $z_0R_0^3$ and zR_0^3 , requiring $\chi_2(1) = 0$ and letting R_0 go to infinity, we have the infinite "hollow" atom discussed previously; and, then, it is easily to see that the equilibrium condition (35) is not satisfied, as it would require $\chi_1(a) = 0$, *i.e.* a vanishing solution. Secondly, we see that if we put $\chi_2(1) = 0$ and $a = 1$ we get again the previous case of an infinite Thomas-Fermi atom, which we know that it is unstable; it follows that even more unstable will be the "hollow" system with $\chi_2(1) = 0$ and $a < 1$, *i.e.* the "positive ion". But we remark that this is only a particular cas of a positive ion.

In the remaining of this paper we shall discuss a few types of solutions for the Thomas-Fermi equation (9) under the boundary conditions (32) – (35), being especially interested in the total charge (36).

For $z_0 = 0$, $R_0 = 2 \text{ \AA}$, $R = 1.73 \text{ \AA}$ ($a = 0.86$) and $z = 44$, as for a (tetrahedral) cluster of four sodium atoms, the function χ is plotted in *Fig.1* vs x ; it corresponds to a total charge $q = +2.7$. For $z_0 = 0$, $R_0 = 3.2 \text{ \AA}$, $R = 2.78 \text{ \AA}$ ($a = 0.87$) and $z = 88$, as for a (cubic) cluster of eight sodium atoms, the function χ is shown in *Fig.2*; the total charge in this case is $q = -0.1$. For $z_0 = 11$, $R_0 = 3.15 \text{ \AA}$, $R = 2.75 \text{ \AA}$ ($a = 0.87$) and $z = 88$, as for a centered (cubic) cluster of nine sodium atoms, the function χ is given in *Fig.3*, for a total charge $q = 0.7$. We remark that, indeed, the function χ has a smoother variation with increasing the number of electrons, except for a range $\sim a_H$ around the positions of atomic charges. In addition, we remark that the charge q is very sensitive to the input parameters, for increasing both the number of electrons and the positive charges.

We may estimate the energy of the system as follows. The density of kinetic electron energy is

$$\varepsilon_{kin} = \frac{2}{(2\pi)^3} 2\pi \int_0^{k_F} dk \frac{1}{2} k^4 = \frac{9(3\pi/32)^3 \chi^{5/2}}{10R_0^{10} x^{5/2}} \quad , \quad (37)$$

whence the total kinetic energy of electrons

$$E_{kin} = \frac{3(3\pi/8)^4}{20R_0^7} \int_0^1 dx \frac{\chi^{5/2}}{x^{1/2}} \quad . \quad (38)$$

The density of potential energy of the electrons is given by

$$\varepsilon_{pot} = -(\varphi + V + U)n = -\frac{3(3\pi/32)^3}{2R_0^{10}} \frac{\chi^{5/2}}{x^{5/2}} - \frac{9\pi}{8^3 R_0^6} \varphi_0 \frac{\chi^{3/2}}{x^{3/2}} \quad , \quad (39)$$

whence their total energy

$$\mathcal{E}_{el} = E_{kin} + E_{pot} = -\frac{(3\pi/8)^4}{10R_0^7} \int_0^1 dx \frac{\chi^{5/2}}{x^{1/2}} - N\varphi_0 \quad , \quad (40)$$

where $N = -(q - z - z_0)$ is the total number of electrons. The energy of the shell is given by

$$\mathcal{E}_s = \mathcal{E}_0 - (z + z_0)U \quad . \quad (41)$$

On the other hand we may express the energy of interaction of the shell with the electrons in two distinct ways

$$\mathcal{E}_i = z\varphi(R) = - \int d\mathbf{r} \, nV \quad , \quad (42)$$

where V is the potential of the shell; from (42) we get

$$U - \varphi_0 = \frac{9\pi^2}{128R_0^4} \chi_2'(1) \quad , \quad (43)$$

which together with (40) and (41) allows one to write the total energy as

$$\mathcal{E} = \mathcal{E}_0 + \mathcal{E}_1 + \mathcal{E}_2 - [2(z + z_0) - q] \varphi_0 \quad , \quad (44)$$

where

$$\mathcal{E}_1 = -\frac{(3\pi/8)^4}{10R_0^7} \int_0^1 dx \frac{\chi^{5/2}}{x^{1/2}} \quad (45)$$

and

$$\mathcal{E}_2 = -\frac{9\pi^2}{128R_0^4} (z + z_0) \chi_2'(1) \quad . \quad (46)$$

In the first case shown in *Fig.1* $\mathcal{E}_1 = -28$, $\mathcal{E}_2 = -42$, $(\chi_2'(1) = 282)$ while the self-energy (4) of the shell is $\mathcal{E}_0 = 297$; for stability, *i.e.* negative total energy, one needs $\varphi_0 \geq (297 - 28 - 42)/88 \sim 2.6$. One can see that, indeed, the object is squeezed into the atomic environment, φ_0 being a measure of the variation of the atomic "pseudo-potential" felt by an outside electron on its attempts of penetrating the electron cloud of the atomic surrounding; these "pseudo-potentials" are potential barriers which confine the clusters. A huge "pressure" is exerted by the cluster on its surrounding, which results in the deformation of the electronic clouds of the cage walls. Similar values are obtained in the other cases, for example, $\varphi_0 \geq (742 - 43 - 92)/176 \sim 3.4$ for eight atoms, and $\varphi_0 \geq (931 - 155 - 110)/200 \sim 2.4$ for nine atoms.

It might be of interest the variation of q with z . For example, we define $Z = 128R_0^3z/9\pi^2$ and $Q = 128R_0^3q/9\pi^2$, and solve the equation for various values of a . Such a dependence of Q on Z is shown in *Fig.4* for $z_0 = 0$ and $a = 0.8$, and in *Fig.5* for $z_0 = 0$ and $a = 0.9$; while in *Fig.6* it is shown an almost neutral cluster for $z_0 = 0$ and $a = 0.87$. Similar results can also be obtained for $z_0 \neq 0$. In *Fig.7* the variation of q with R_0 is shown for $z_O = 0$, $z = 44$ and $R = 1.73 \text{ \AA}$, while in *Fig.8* a similar dependence is included for $z_O = 11$, $z = 88$ and $R = 2.75 \text{ \AA}$.

In the limit of large number of atoms in the cluster the Thomas-Fermi theory is valid. For a finite number n of atoms disposed on a spherical surface one may estimate the error in the total charge as follows. From the Poisson equation we have that the charge q is proportional to the radial $\delta\varphi_r'$ and angular $\delta\varphi_a'$ variations of the potential derivatives in the following way:

$$q \sim \delta\varphi_r' \Delta S + 2\delta\varphi_a' \Delta S \quad , \quad (47)$$

where ΔS is the element of area. Assuming the same variation per unit length we find

$$\delta\varphi_a' = \delta\varphi_r' \sqrt{\frac{4\pi}{n}} \quad . \quad (48)$$

On the other hand, if one neglects the angular variations we have

$$q_0 \sim (\delta\varphi_r')_0 \Delta S \quad . \quad (49)$$

As these small variations are proportional to the small variations of the distance we should also have

$$(\delta\varphi_r')^2 + 2(\delta\varphi_a')^2 = (1 + 8\pi/n) (\delta\varphi_r')^2 = (\delta\varphi_r')_0^2 \quad , \quad (50)$$

whence

$$\Delta q/q \sim 1 - \frac{\sqrt{1 + 8\pi/n}}{1 + 2\sqrt{4\pi/n}} \quad . \quad (51)$$

In our cases of $n \sim 4, 8, 9$ this error in Δq is about 40%.

References

- [1] See, for example, J. Cioslowski, *Electronic Structure Calculations on Fullerenes and Their Derivatives*, Oxford (1995).
- [2] See, for example, W. A. de Heer, *Revs. Mod. Phys.* **65** 611 (1993) and M. Brack, *ibid* 677.

Figure captions

Fig.1.

Function χ vs x for $z_0 = 0$, $R_0 = 2 \text{ \AA}$, $R = 1.73 \text{ \AA}$ ($a = 0.86$) and $z = 44$,
and

a total charge $q = +2.7$.

Fig.2.

Function χ vs x for $z_0 = 0$, $R_0 = 3.2 \text{ \AA}$, $R = 2.78 \text{ \AA}$ ($a = 0.87$) and
 $z = 88$,
and a total charge $q = -0.1$.

Fig.3.

Function χ vs x for $z_0 = 11$, $R_0 = 3.15 \text{ \AA}$, $R = 2.75 \text{ \AA}$ ($a = 0.87$) and
 $z = 88$,
and a total charge $q = 0.7$.

Fig.4.

The reduced charge Q vs Z for $z_0 = 0$ and $a = 0.8$.

Fig.5.

The reduced charge Q vs Z for $z_0 = 0$ and $a = 0.9$.

Fig.6.

The reduced charge Q vs Z for $z_0 = 0$ and $a = 0.87$ for an almost neutral
cluster.

Fig.7.

The total charge q vs R_0 for $z_0 = 0$, $z = 44$, and $R = 1.73 \text{ \AA}$.

Fig.8.

The total charge q vs R_0 for $z_0 = 11$, $z = 88$, and $R = 2.75 \text{ \AA}$.